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(21) International Application Number: PCT/US98/20619 (22) International Filing Date: 29 September 1998 (29.09.98) (30) Priority Data: 08/939,712 29 September 1997 (29.09.97) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/939,712 (CIP) Filed on 29 September 1997 (29.09.97) (71) Applicant (for all designated States except US): CREATIVE PRODUCTS RESOURCE, INC. [US/US]; 41 Plymouth Street, Fairfield, NJ 07004 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): SMITH, James, A. [US/US]; 85 Watch Hill Way, Chatham, MA 02633 (US). (74) Agents: PAULSON, Mark, G. et al.; Cushman Darby & Cushman, Intellectual Property Group of, Pillsbury Madison & Sutro, 1100 New York Avenue, N.W., Washington, DC 20005 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DRY-CLEANING KITS INCLUDING COMPOSITIONS CONTAINING POLYSULFONIC ACID (57) Abstract This invention relates to dry-cleaning systems which include anhydrous dry-cleaning compositions which contain polysulfonic acid, and a bag for the cleaning and containment of soiled fabric articles. In a first embodiment, the dry-cleaning compositions include organic solvents, polysulfonic acid, and not more than about 10 wt.% water. In a second embodiment, the dry-cleaning compositions include organic solvents and polysulfonic acid, and not more than about 1 wt.% water. The invention also relates to methods of using the dry-cleaning system and dry-cleaning composition.		

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DRY-CLEANING KITS INCLUDING COMPOSITIONS CONTAINING POLYSULFONIC ACID

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FIELD OF THE INVENTION

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The present invention relates to anhydrous dry-cleaning systems utilizing polysulfonic acid, by which delicate fabric articles can be freshened or dry-cleaned in a dryer, such as a rotary clothes dryer. The invention includes such dry-cleaning compositions and bags having an opening with a fastening system that enables closure of the bag in a vapor impermeable manner. The invention also contemplates kits containing the dry-cleaning compositions and the bags, as well as methods for using the dry-cleaning systems.

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BACKGROUND OF THE INVENTION

Methods for dry-cleaning fabrics commonly employ organic solvents which can readily dissolve or disperse soils such as water-insoluble substances, including greases, oily dirt and the like, and which exhibit low solvent boiling points, enabling easy recovery of the solvents.

The use of solvent-based dry-cleaning methods has, however, been primarily limited to commercial cleaning operations which employ expensive specialized equipment. Such equipment

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includes stills with condensers to contain vapors from the cleaning solvents, which are often toxic. As a result, to utilize such dry-cleaning processes, particularly to remove water-insoluble spots and/or stains from clothes, the user must bring the clothes to a specialized dry-cleaning establishment and pick up the cleaned clothes at a later date. This results in inconvenient expenditures of time in going to the dry-cleaner, waiting for the clothes to be properly cleaned, picking up the clothes, and dealing with damaged and lost articles of clothing. Moreover, articles of clothing from many different people are dry-cleaned with the same batch of solvent, which can result in malodorous residues.

A process for home dry-cleaning clothing is disclosed by S. Denissenko et al. in U.S. Patent No. 4,336,024, wherein the soiled areas are pre-treated with a liquid cleaning composition. The clothing is then attached to an absorbent sheet and spun using the spin cycle of a washing machine, so that the cleaning composition and the soil are driven through the clothing and into the absorbent sheet. It is also disclosed that the absorbent sheet can be integrally sealed onto a plastic sheet, so that the clothing can be enclosed by the sheet while it is spun in a washing machine. Also, U.S. Patent No. 5,238,587 issued to J. Smith et al., discloses a method for cleaning soiled fabric via the enclosure of the desired clothing in a bag with an added sheet impregnated with a gelled liquid cleaning composition. (The entire contents of U.S. Patent No. 4,336,024 and U.S. Patent No. 5,238,587 are incorporated herein by reference.)

However, these conventional methods for dry-cleaning contain high amounts of water as a

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component. High water level formulations tend to leave "water marks" after the spot or stain is removed from soiled fabrics, especially delicate fabrics such as 100% acetate, silk, rayon and blends of these fabrics. In fact, these delicate fabrics (especially acetate and rayon) will simply water stain from exposure to rain. To combat this problem, current professional dry cleaning methods use essentially anhydrous solvent systems based on perchloroethylene or hydrocarbon solvents, which are undesirable from an environmental standpoint. Such professional systems also contain detergents (usually about 1 - 3%) and a small amount of water (about 5%) to help the detergents work.

It is therefore an object of the invention to provide a dry-cleaning composition that contains no or only small amounts of water when compared to conventional dry-cleaning compositions.

It is an object of the invention to provide a dry-cleaning composition that contains polysulfonic acid as an essential ingredient.

It is an object of the invention to provide a dry-cleaning composition suitable for use in dry-cleaning delicate fabrics such as 100% acetate, silk, rayon and blends of these fabrics.

It is also an object of the invention to provide such a dry-cleaning composition that does not include solvents like perchloroethylene or other undesirable hydrocarbon solvents, such as those used commercially.

It is an object of the invention to provide methods of use therefor which can be conducted at home without having to take soiled or stale-smelling clothes to commercial cleaning establishments and incurring such inconveniences and disadvantages mentioned above.

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Additional objects of the present invention will become readily apparent to persons skilled in the art from the following discussion.

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SUMMARY OF THE INVENTION

The present invention provides anhydrous dry-cleaning or fabric-freshening systems adapted for dry-cleaning and/or freshening all types of fabric articles, but especially for delicate
10 fabric articles (such as, for instance, 100% acetate, 100% silk, 100% rayon and blends of these fabrics).

In a first embodiment, the system uses an effective amount of a dry-cleaning composition
15 consisting essentially of

at least 1 water-miscible or partially water-miscible organic solvent;
polysulfonic acid; and

water. The amount of water should not
20 exceed about 10 weight percent of the total dry-cleaning composition, and preferably does not exceed about 6 weight percent (although the amount of water can be as low as about 0 weight percent).

Preferably the organic solvent is non-
25 polar, and is preferably selected from the group consisting of dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, tripropylene glycol methyl ether, 3-methoxy-3-methyl-1-butanol and γ -butyrolactone. Preferably the organic
30 solvent is present between about 85 and about 98.5 total weight percent based on the total weight percent of the composition, although total amounts may vary as desired and depending on the presence of other components, as described below, as would
35 be understood by someone of ordinary skill in this art. Preferably the polysulfonic acid is present in an amount effective to stabilize the organic

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solvent in the dry-cleaning composition and to promote the distribution of the dry-cleaning composition on delicate fabric articles while leaving no significant undesirable visible residue on the delicate fabric article (preferably between about .5 and about 5 total weight percent based on the total weight percent of the composition). Preferably, the water is present in an effective amount to disperse the polysulfonic acid (preferably between about 1 and about 6 weight percent water, based on the total weight percent of the composition).

In a preferred composition of this embodiment, the dry-cleaning composition consists essentially of about 95% of the at least 1 organic solvent, about 2.5% of polysulfonic acid, and about 2.5% water.

In a second embodiment, the dry-cleaning system uses an effective amount of a dry-cleaning composition consisting essentially of

at least 1 organic solvent (preferably non-polar); and polysulfonic acid. In this embodiment, the amount of water present should be as close to 0 weight percent as possible. The organic solvent should be present in an effective amount to disperse the polysulfonic acid in the absence of sufficient water to do so (preferably between about 90 and about 99.9 weight percent organic solvent, based on the total weight percent of the composition). Suitable organic solvents for this purpose include tripropylene glycol methyl ether, (2-(2-ethoxy)ethoxy)ethanol, and other functional equivalents, especially those in the glycol ether family.

Preferably the polysulfonic acid is present in an amount effective to stabilize the

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organic solvent in the dry-cleaning composition and to promote the distribution of the dry-cleaning composition on fabric articles while leaving no significant undesirable visible residue
5 on the fabric article (preferably between about 0.1 and about 10 total weight percent, based on the total weight percent of the composition).

In a preferred composition of this second embodiment, the dry-cleaning composition
10 consists essentially of about 97.5% of the at least 1 organic solvent, and about 2.5% of polysulfonic acid.

The above-described first and second embodiments of the dry-cleaning compositions may
15 further include other components that do not interfere with the dry-cleaning activity of the compositions. For instance, the compositions may include surfactants, which if present are preferably in an amount between about .01 and
20 about 10 weight percent, based on the total weight percent of the composition.

The above-described first and second embodiments of the dry-cleaning compositions may further include gelling agents or viscosity
25 modifiers. In addition, the above-described dry-cleaning compositions may further include fabric-softening agents, or other desired agents.

The above-described first and second embodiments of the dry-cleaning compositions may
30 be present on a substrate (for instance, a sheet, a sponge, a dauber, a stick, granules or a cube). A sheet is the preferred substrate, such as, for instance, a plastic sheet or a porous sheet, and the dry-cleaning composition may be stably
35 impregnated onto the sheet. Advantageously, the dry-cleaning compositions of this invention remain in a moist or wet state when present on a

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substrate, which is an unusual property in that the compositions contain so little (or no) water. In the alternative, the dry-cleaning compositions may be present in a spray or roll on solution, or
5 the like.

The invention also relates to the above-described dry-cleaning systems which further include a bag that has an opening comprising a fastening system so that the bag can enclose the
10 soiled fabric article in an effective vapor impermeable manner. One option with this form of the invention, instead of or in addition to placing into the bag an effective amount of the dry-cleaning composition, is that the bag has an
15 interior surface, and at least a portion of the interior surface has an effective amount of the dry-cleaning composition releasably absorbed thereinto, wherein the bag is formed of a flexible non-porous material which is not substantially
20 damaged upon exposure to agitation and to a temperature effective to cause the release of the dry-cleaning composition from the interior surface.

The invention also relates to processes
25 for cleaning or freshening a soiled fabric article with the above-described dry-cleaning systems. Such processes comprise the steps of

(a) placing into a bag the soiled fabric article and an effective amount of at least
30 one of the above-described first or second embodiment of the dry-cleaning compositions,

wherein the bag includes an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective
35 vapor impermeable manner;

(b) closing the fastening system to form the bag into an effective closed system

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comprising the soiled fabric article and the dry-cleaning composition;

(c) tumbling the closed system in a rotary clothes dryer at an elevated temperature, so that the dry-cleaning composition contacts the soiled fabric article so as to effectively disperse the soil; and

(d) opening the fastening system and removing the cleaned or freshened fabric article from the bag.

The invention also relates to methods for removing a stain from a soiled fabric article with the above-described dry-cleaning systems. Such methods comprise the steps of

(a) placing into a bag the soiled fabric article and an effective amount of at least one of the above-described first or second embodiment of the dry-cleaning compositions,

wherein the bag includes an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner;

(b) closing the fastening system to form the bag into an effective closed system comprising the soiled fabric article and the dry-cleaning composition;

(c) tumbling the closed system in a rotary clothes dryer at an elevated temperature, so that the dry-cleaning composition contacts the soiled fabric article so as to effectively disperse the stain; and

(d) opening the fastening system and removing the cleaned fabric article from the bag. If desired, prior to step (a), an amount of the dry-cleaning composition may be applied to the soiled fabric article to loosen the stain (for instance, by rubbing or dabbing the soiled fabric

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article with the dry-cleaning composition, or by spraying, rolling on or dipping the soiled fabric article with the dry cleaning composition).

5 The invention also relates to kits for dry-cleaning or fabric-freshening a fabric article. These kits comprise, packaged in association,

10 (i) an effective amount of at least one of the above-described first or second embodiment of the dry-cleaning compositions, and

(ii) a bag including an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner. The bag may include an interior surface such as is described above, wherein at least a portion of the interior surface has an effective amount of the dry-cleaning composition releasably absorbed thereinto.

20 The present invention, including the above-described embodiments and preferred versions thereof is more fully described in the following detailed discussion, wherein all percentages are by weight of the total cleaning composition, unless otherwise noted.

25

DETAILED DESCRIPTION OF THE INVENTION

As discussed above, the present invention provides dry-cleaning or freshening systems for dry-cleaning or freshening fabric articles, comprising an anhydrous dry-cleaning composition including polysulfonic acid, and, preferably, a bag. The term "anhydrous" as used herein encompasses compositions that have no water or low water content (especially when compared to conventional dry-cleaning compositions), such that when used for dry-cleaning purposes the

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composition will leave little or no water stains on fabrics treated therewith (especially delicate fabrics). For instance, the compositions generally will contain not more than about 5% by weight, and in any case not more than about 10% by weight.

The term "fabrics" or "fabric articles" encompasses not only clothing, but other items which are commonly dry-cleaned, including sheets, draperies, rugs, upholstery coverings, towels and the like. For this invention, the term "fabrics" also can include delicate fabrics, such as 100% acetate, silk, rayon and blends of these fabrics.

As used herein, the term "dryer" refers to a rotary hot air dryer, which tumbles the clothes in a drum with warm or heated air at an elevated temperature, usually at a temperature of about 40 and about 95°C, preferably at about 50 and about 90°C, for preselected periods of time (preferably, between about 15 and about 45 minutes).

As used herein with respect to the fabrics to be dry-cleaned or freshened, the term "soil" includes odoriferous compounds such as tobacco smoke, residue, perfume, mustiness, perspiration and the like, as well as visible spots and stains.

Therefore, as used herein, the term "freshen" includes the removal, deodorizing, chemical neutralizing and/or masking of odoriferous compounds on or within a fabric with a desirable scent. As used herein, the term "dry cleaning" or "cleaning" includes the removal of both kinds of "soil".

In the practice of the present invention, an effective amount of one or both of the above-described first or second embodiments of

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the dry-cleaning compositions is contacted with the soiled fabric (or fabrics). The composition contacts spotted and/or stained portions of fabric therein and removes or decreases the spots and/or stains. In addition to, or in the alternative, the composition contacts the fabric and freshens it.

The compositions of this invention work most effectively when subjected to heat. Therefore, in the preferred practice of the invention, the soiled fabric (or fabrics) is added to the bag along with an effective amount of at least one of the above-described dry-cleaning compositions, and the bag is subjected to an amount of agitation and heat effective to release the dry-cleaning composition in liquid and/or in vaporous form from the substrate, vehicle, fabric, interior absorptive surface of the bag, etc., on which the dry-cleaning composition is present in the bag. The composition in liquid and/or vaporous form contacts the fabric article and cleans it. Moreover, the composition contacts spotted and/or stained portions of fabric therein and removes or decreases the spots and/or stains. In addition to, or in the alternative, the composition contacts the fabric and freshens it.

In a preferred aspect of the invention, the bag of the present invention may be placed in a rotary hot air clothes dryer to provide the effective amount of heat and agitation, or tumbling. Thus, the present invention provides a method for cleaning and/or freshening soiled fabric articles comprising (a) placing a soiled fabric article (i.e., spotted, stained and/or in need of freshening) in the aforesaid dry-cleaning bag; (b) sealing the bag; and (c) tumbling the sealed bag and its contents in a dryer at a

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temperature effective to release the anhydrous dry-cleaning composition in liquid and/or vapor form and for a time effective to contact an effective amount of the released dry-cleaning composition with the soiled fabric, so as to clean and/or freshen the fabric.

A. Organic solvents

All the embodiments of the present anhydrous dry-cleaning compositions contemplate organic solvents. Where water is a required component in the dry-cleaning composition, as for instance in the above-described first embodiment, the organic solvent should be water-miscible, or at least partially water-miscible. As would be understood by someone skilled in this art, the less water that is present in the composition, the lower the polarity of the organic solvent is preferred.

Preferably, the major portion of the organic solvent can be a glycol ether. These materials are lower(alkoxy)- or lower(alkoxy)lower(alkoxy)-ethers of ethanol or isopropanol. Some examples of preferred glycol ethers are available under the trade names Arcosolv® (Arco Chemical Co.) or Cellosolve®, Carbitol®, or Propasol® (Union Carbide Corp.), and include, e.g., butylCarbitol®, hexylCarbitol®, methylCarbitol®, and Carbitol® itself, (2-(2-ethoxy)ethoxy)ethanol.

Where water is a required component in the dry-cleaning composition, as for instance in the above-described first embodiment, the more preferred organic solvents include dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, tripropylene glycol methyl ether, 3-

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methoxy-3-methyl-1-butanol and γ -butyrolactone. Certain of these solvents, including 3-methoxy-3-methyl-1-butanol and γ -butyrolactone, are preferably used in combination with at least one
5 other solvent. When γ -butyrolactone is the solvent used it is preferably used in small amounts and mixed with another organic solvent.

Other glycol ethers useful in the invention include diethylene glycol monobutyl
10 ether, triethylene glycol monobutyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, dipropylene glycol monobutyl ether, butylethoxypropylene glycol, diethylene glycol monomethyl ether, triethylene glycol
15 monomethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monopropyl ether, diethylene glycol monopropyl ether, ethylene glycol monobutyl ether, propylene glycol monomethyl ether,
20 dipropylene glycol monomethyl ether, propylene glycol monopropyl ether, propylene glycol monobutyl ether, propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol n-propyl ether, propylene glycol t-butyl ether,
25 propylene glycol n-butyl ether, dipropylene glycol methyl ether, dipropylene glycol t-butyl ether, dipropylene glycol n-butyl ether, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether, ethylene glycol
30 butyl ether, ethylene glycol hexyl ether, ethylene glycol ethyl hexyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol propyl ether, diethylene glycol butyl ether, tripropylene glycol n-butyl ether,
35 propylene glycol phenyl ether, propylene glycol n-phenyl ether, ethylene glycol n-butyl ether, diethylene glycol n-butyl ether, triethylene

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glycol butyl ether, triethylene glycol methyl ether, ethylene glycol phenyl ether, aromatic-based glycol ethers, and mixtures thereof. Such glycol ethers are commercially available, for instance, from Dow, Union Carbide and Arco. Of course, the choice of glycol ether can be readily made by one of ordinary skill in the art on the basis of its volatility, wt-% of the total dispersion and the like.

It is noted that certain solvents are probably not useful, especially with respect to the above-described second embodiment of the dry-cleaning compositions, because these solvents can dissolve or stain 100% acetate fabrics. Such solvents include N-methyl-2-pyrrolidone, γ -butyrolactone, methoxytriglycol, and propylene carbonate.

Alcohols which can be employed as co-solvents include liquid polyethylene glycols, i.e., polyethylene glycol-200, 300, 400 or 600, wherein the suffixed numbers indicate the approximate molecular weight of the glycol. Other useful co-solvents include other alcohols, for example, C₂-C₄ polyols, such as a diol or triol, e.g., ethylene glycol, propylene glycol, glycerol or mixtures thereof.

Other organic solvents can also be used in addition to the at least one organic solvent required in the compositions of the invention, including conventional chlorinated dry-cleaning solvents. Preferred examples of these solvents comprise the di- to tetrachlorinated derivatives of methane, the di- to pentachlorinated derivatives of ethane and of ethylene, the mono- to trichlorinated derivatives of cyclohexane, and monochlorobenzene. Specific examples of this type include carbon tetrachloride, methylenechloride,

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1,1-dichloroethane, 1,2-dichloroethane,
1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1-
-trichloroethane, 1,1,2-trichloroethane,
trichloroethylene, 1,1,2,2-tetrachloroethane,
5 tetrachloroethylene, pentachloroethane,
monochlorocyclohexane, 1,4-dichlorocyclohexane,
monochlorobenzene and mixtures of the foregoing.
Further, hydrocarbon solvents such as
isoparaffinic solvents (available commercially as
10 Isopar K and DP-2000) can be useful.

B. Polysulfonic acid and water

All of the embodiments of the present
anhydrous dry-cleaning compositions contemplate
15 polysulfonic acid as a critical component.

Polysulfonic acid is a polymer which is
17% active in water and has a high viscosity (more
than about 20,000 cps). It has been determined
that polysulfonic acid affords special advantages
20 when present in the anhydrous dry-cleaning
compositions described herein. For instance,
polysulfonic acid acts as a surfactant and
exhibits stain removal properties, adds slip
characteristics to fabrics (e.g., reduction in
25 drag), and helps dissolve/disperse the other
components of the composition onto the fabric
without leaving a white residue. The inclusion of
polysulfonic acid allows the composition to be
effective for dry-cleaning with only a minimum
30 amount of water (e.g., less than about 10% water),
and even in compositions that contain no water at
all.

Because polysulfonic acid is generally
not dispersible or dissolvable in most organic
35 solvents, a small amount of water is often needed
in order to disperse the polysulfonic acid and
build sufficient viscosity with it. This is the

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case in the above-described first embodiment of the dry-cleaning compositions, and the preferred water content contemplated is between about 1 and about 6 weight percent (although more water could be present without detrimental effect to the properties or usefulness of the polysulfonic acid). The small amount of water should not be enough to water-stain the fabrics, but should be sufficient to disperse the polysulfonic acid and build sufficient viscosity. The presence of the water is also useful to enhance the cleaning and other beneficial properties of the polysulfonic acid and, if added, surfactants. Preferably, the level of water to polysulfonic acid is such that the resulting product is a clear slightly viscous composition. Another advantage of the presence of water is that it helps suppress the flash point of the organic solvent, and therefore makes the dry-cleaning systems safer for general use.

As in the case of the above-described second embodiment, it is possible to disperse and build sufficient viscosity with the polysulfonic acid with certain organic solvents, in the absence of any water at all. Suitable organic solvents for this purpose are described above.

Polysulfonic acid is commercially available from, for example, Henkel under the name HSP-1180.

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C. Fabric-treatment agents and other additives

In all of the embodiments of the invention, the above-described dry-cleaning compositions may further include fabric-softening agents, or other desired agents. The dry-cleaning compositions of the invention contemplate any type of fabric-treatment agent, as long as such

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additives do not interfere with the dispersal and spot and/or stain removal properties of the composition. The compositions may also, or in the alternative, include an agent selected from the group consisting of anti-creasing agents, anti-soil agents, bacteriostatic agents, brightening agents, bodying agents, dyes, coloring agents, fiber emollients, finishing agents, fragrances, germicides, lubricants, mildew-proofing agents, moth-proofing agents, shrinkage controllers, preservatives, fiber emollients, stain-removing agents, deodorants, insect repellents, sizing agents, and the like, and mixtures thereof.

The above-described first and second embodiments of the dry-cleaning compositions may further include a compound having a vapor tension of less than or equal to 4 Pa at 25°C, which is selected from the group consisting of C₁₀-C₁₂ aliphatic alcohols, C₁₀-C₁₃ aldehydes, C₁₃-C₁₈ aliphatic ketones, aromatic ketones having a musk odor and up to 18 carbon atoms, C₈-C₁₅ aliphatic esters, methyl anthranilate, methyl N-methylanthranilate, p-cresyl phenylacetate, amyl salicylate, coumarin, dihydrocoumarin, gammadecalactone, dodecalactone, undecalactone, eugenol, isoeugenol, diphenyl oxide, the methyl and ethyl ethers of naphthol, galaxolide, indole and its reaction products with hydroxycitronella, tridecene-2-nitrile, and 2-(2'-methyl-pent-2'-enyl)-5-methyl pyridine. Such compounds are described in Joulain et al., U.S. Patent No. 4,840,792 (the entire content of which is incorporated herein by reference).

The fabric-treatment agent can include minor but effective amounts of one or more surfactants. The surfactants act as cleaning intensifiers to facilitate removal of the soil

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upon release of the dry-cleaning composition in the dryer. Surfactants are useful in the dry-cleaning composition in amounts from about .01 to about 10 weight percent.

5 Non-ionic surfactants and amphoteric surfactants are preferred for use in the dry-cleaning composition and can also act as adjunct fabric softeners. Minor but effective amounts of certain anionic surfactants may also be
10 useful to provide faster dissipation of the composition in the dryer.

Nonionic surfactants contemplated by the invention include the condensation products of ethylene oxide with a hydrophobic polyoxyalkylene
15 base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds has a molecular weight sufficiently high so as to render it water-insoluble. Where appropriate, the addition
20 of polyoxyethylene moieties to this hydrophobic portion increases the water-solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total
25 weight of the condensation product. Examples of compounds of this type include certain of the commercially-available Pluronic® surfactants (BASF Wyandotte Corp.), especially those in which the polyoxypropylene ether has a molecular weight of
30 about 1500-3000 and the polyoxyethylene content is about 35-55% of the molecule by weight, i.e., Pluronic® L-62.

Preferred nonionic surfactants include the condensation products of C₈-C₂₂ alkyl alcohols
35 with 2-50 moles of ethylene oxide per mole of alcohol. Examples of compounds of this type include the condensation products of C₁₁-C₁₅ fatty

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alcohols with 3-50 moles of ethylene oxide per mole of alcohol which are commercially available from Shell Chemical Co., Houston, TX, as, i.e., Neodol® 23-6.5 (C₁₂-C₁₃ fatty alcohol condensed with about 7 moles of ethylene oxide), the PolyTergent® SLF series from Olin Chemicals or the Tergitol® series from Union Carbide, i.e., Tergitol® 15-S-15, which is formed by condensing about 15 moles of ethylene oxide with a C₁₁-C₁₅ secondary alkanol; Tergitol® TMN-6, which is the condensation product of about 6 moles of ethylene oxide with isolauryl alcohol. (CTFA name: isolaureth-6); Incropol® CS-12, which is a mixture of stearyl and cetyl alcohol condensed with about 12 moles of ethylene oxide (Croda, Inc.); Incropol® L-7, which is lauryl alcohol condensed with about 7 moles of ethylene oxide (Croda, Inc.); and Tergitol® 15-S-3, which is the condensation product of about 3 moles of ethylene oxide with a mixture of (C₁₁-C₁₅) secondary alcohols.

Preferred nonionic surfactants also include (C₈-C₂₄) fatty acid amides, e.g., the monoamides of a mixture of arachidic and behenic acid (Kenamide® B, Humko Chem. Co., Memphis, TN), and the mono- or di-alkanolamides of (C₈-C₂₂) fatty acids, e.g., the diethanol amide, monoethanol amide or monoisopropanolamide of coconut, lauric, myristic or stearic acid, or mixtures thereof. For example, Monamidet® S is the monoethanol amide of stearic acid (Mona Industries, Inc., Patterson, NJ), and Monamine ALX-100S (Mona Industries), is a mixture of the diethanol amide of cocoa fatty acid and the diethanol amide of dodecylbenzene sulfonic acid. The fatty alkanolamide designated "Active #2" (Blew Chem. Co.) is also believed to be of this class of nonionic surfactant.

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Other nonionic surfactants which may be employed include the ethylene oxide esters of C₆-C₁₂ alkyl phenols such as (nonylphenoxy)polyoxyethylene ether. Particularly useful are the esters prepared by condensing about 8-12 moles of ethylene oxide with nonylphenol, i.e., the Igepal® CO series (Rhone-Poulenc, Cranbury, N.J.).

Other useful nonionics include the ethylene oxide esters of alkyl mercaptans such as dodecyl mercaptan polyoxyethylene thioether, the ethylene oxide esters of fatty acids such as the lauric ester of polyethylene glycol and the lauric ester of methoxypolyethylene glycol, the ethylene oxide ethers of fatty acid amides, the condensation products of ethylene oxide with partial fatty acid esters of sorbitol such as the lauric ester of sorbitan polyethylene glycol ether, and other similar materials, wherein the mole ratio of ethylene oxide to the acid, phenol, amide or alcohol is about 5-50:1.

Useful amphoteric surfactants include the (C₈-C₂₂) alkyl(dimethyl)amine oxides, such as those of the Schercamox® series (Scher Chem. Co., Clifton, NJ), e.g., Schercamox DML is lauryl(dimethyl)amine oxide. Other useful amphoteric surfactants are known to the art, e.g., as disclosed in Marshall et al. U.S. Patent No. 3,936,538), the disclosure of which is incorporated by reference herein.

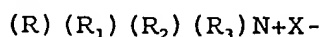
Anionic surfactants suitable for use in the dry-cleaning composition are well known to those of skill in the art, and include, for example, sodium cocoyl isethionate, commercially available as Jordapon®CI from Mazer Chemicals, Gurnee, Illinois. The anionic surfactant may be optionally added in minor but effective amounts

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e.g., up to about 1%, in addition to the nonionic or amphoteric surfactant.

One broad class of cationic surfactants suitable for use in the dry-cleaning compositions is referred to as quaternary amines, or "quats." These materials not only function to facilitate soil removal, but can also function to condition the fabrics and to reduce static cling and lint adherence. Subclasses of these materials are well known to those of skill in the art and include the monomethyl trialkyl quaternaries, imidazolinium quaternaries, dimethyl alkyl benzyl quaternaries, dialkyl dimethyl quaternaries, methyl dialkoxy alkyl quaternaries, diamido amine-based quaternaries and dialkyl methyl benzyl quaternaries preferably the "alkyl" moiety of these compounds is a (C₈-C₂₄) alkyl group and the quaternary(amine) is a chloride or methosulfate salt.

It is sometimes preferable, for convenience, to define the subclasses of aliphatic quaternary amines suitable for use in the dry-cleaning compositions structurally. For example, one useful subclass of aliphatic quaternary amines may be structurally defined as follows:



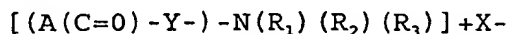
wherein R is benzyl, or lower(alkyl) benzyl; R₁ is alkyl of 10 to 24, preferably 12 to 22 carbon atoms; R₂ is C₁₀-C₂₄-alkyl, C₁-C₄-alkyl, or (C₂-C₃)hydroxyalkyl, R₃ is C₁-C₄-alkyl or (C₂-C₃)hydroxyalkyl and X represents an anion capable of imparting water solubility or dispersibility including chloride, bromide, iodide, sulfate and methosulfate. Particularly preferred species of these aliphatic quats include n-C₁₂-C₁₈-alkyl-dimethylbenzylammonium chloride

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(myrisalkonium chloride), n-C₁₂-C₁₄-alkyldimethyl(ethylbenzyl) ammonium chloride (quaternium 14), dimethyl-(benzyl)ammonium chloride and mixtures thereof. These compounds are commercially available as, for instance, Variquat® B-343 from Sherex Chem. Co., Dublin, OH which is a dihydrogenated tallow methyl benzyl ammonium chloride. This class of quat is germicidal, and is preferably used in combination with at least one of the other quats disclosed hereinbelow.

Other useful aliphatic quats include those wherein both R and R₁ are (C₈-C₂₄)alkyl, e.g., the N,N-di-(higher)-C₁₀-C₂₄-alkyl-N,N-di(lower)-C₁-C₄(alkyl)quaternary ammonium salts such as distearyl(dimethyl)ammonium chloride, dihydrogenated tallow(dimethyl)ammonium chloride, ditallow(dimethyl)ammonium chloride (Arquad® 2HT-75, Akzo Chemie, McCook, IL), distearyl(dimethyl)ammonium methylsulfate and di-hydrogenated-tallow(dimethyl)ammonium methyl sulfate (Varisoft® 137, Sherex).

Other useful quaternary ammonium antistatic agents include the acid salts of (higher(alkyl)-amido(lower)alkyl)-(dialkyl)-amines of the general formula:



wherein A is a C₁₄-C₂₄ normal or branched alkyl group, Y is ethylene, propylene or butylene, R₁ and R₂ are individually H, C₁-C₄(lower)alkyl or (C₁-C₃)hydroxyalkyl or together form the moiety -CH₂-CH₂YCH₂-CH₂-, wherein Y is NH, O or CH₂; R₃ is the same as R₁ or is also [A(C=O)Y-], and X is the salt of an organic acid. Compounds of this class are commercially available from Croda, Inc., New York, NY, as the Incromate® series, e.g., Incromate® IDL [isostearamidopropyl(dimethyl)amine lactate], Incromate® ISML [isostearamidopropyl

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(morpholinium)lactate] and Incromate® CDP [cocamidopropyl(dimethyl)amine propionate], or as Incrosoft® T-75 [Ditallowdiamido methosulfate (quaternium 53)].

5 Examples of preferred imidazolinium quaternaries include, but are not limited to, (methyl-1-tallow-amido)ethyl-2-tallow imidazolinium methyl sulfate, available commercially from Sherex Chemical Co. as Varisoft®
10 475; (methyl-1-oleylamido)ethyl-2-oleyl-imidazolinium methyl sulfate, available commercially from Sherex Chemical Co. as Varisoft® 3690; tallow imidazolinium methosulfate (Incrosoft® S-75), and alkylimidazolinium
15 methosulfate (Incrosoft® CFI-75), both available from Croda, Inc., New York, NY.

Other useful amine salts are the stearyl amine salts that are soluble in water such as stearyl-dimethylamine hydrochloride, distearyl
20 amine hydrochloride, decyl pyridinium bromide, the pyridinium chloride derivative of the acetylaminioethyl esters of lauric acid, lauryl trimethyl ammonium chloride, decylamine acetate and bis[(oleoyl)-(5,8)-ethanoloxyl]-tallow
25 (C₁₄-C₁₈)aminehydrogen phosphate (Necon® CPS-100) and the like.

Other optional additives for all of the embodiments of this invention are gelling agents and viscosity modifiers. When employed, the
30 gelling agent or viscosity modifier is effective to thicken and otherwise decrease viscosity the dry-cleaning composition. Preferably, the gelling agent comprises an organic gelling agent. For instance, useful dispersing agents can include
35 modified starches, fatty acid and acid salts and fatty alcohols.

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When the above-described second embodiment of the dry-cleaning composition is used, the gelling agent is preferably fumed silica (commercially available under the name of Cabosil). Fumed silica is also useful in controlling the volatility of the dry-cleaning composition when it is released from the substrate. . However, one should keep in mind that fumed silica sometimes leaves residues on fabrics when attempting to remove spots therefrom, and consequently care should be exercised when using it with the dry-cleaning compositions.

When employed, the compositions will preferably contain about 0.25 - to about 8% of the gelling agent or viscosity modifiers. Fumed silica is capable of thickening the compositions at about 3 to about 5 wt.%.

20 D. Applications of the dry-cleaning compositions

The anhydrous dry-cleaning compositions of the invention may be applied to soiled fabric articles in any manner that does not significantly interfere with the necessary functions of the various components of the composition. Preferably, the dry-cleaning composition is present in the dry-cleaning system on a substrate. For instance, the substrate may be a sheet, a sponge, a dauber, a stick, a cube, granules or the like.

30 A sheet is the preferred substrate. Fabric materials useful to form the sheet (which should be flexible) are woven or, preferably, non-woven fibers that are generally adhesively or thermally bonded. Fibrous sheets having a web or corded fiber structure, or those which comprise fibrous mats in which the fibers are distributed haphazardly or in a random array can also be used.

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The fibers can be natural, such as wool, silk, jute, hemp, cotton, linen, sisal, or ramie; or synthetic such as rayon, cellulose ester, polyvinyl derivatives, polyolefins, polyamides or polyesters. Generally, any diameter or denier of fiber is useful in the present invention. The non-woven cloth materials employed herein are not prone to tear or separate when used, for example, in an automatic dryer, due to the haphazard or random array of fibers in the non-woven material which impart excellent strength in all directions. Some examples of preferred non-woven cloth material useful as substrates in the present invention include 100% rayon sheets, known as Fabray® Nonwoven Fabric F-110 (40 gm), available from Sterns Technical Textile Co.; or 100% polypropylene sheets, known as NW-161, available from Kimberly Clark Co., Neenah, WI; or as #405 or #498 from Fiber Dynamics; or as Grade 10180, 10244 or 23102 from Dexter Non-Wovens Division (blended from cellulosic rayon and synthetic fibers); or as Style 778 from Speciality Textiles.

Preferably the sheets have dimensions ranging from about 3" X 4" up to about 14" X 16". However, the sheet must also be of a sufficient size to carry a desirable load of dry-cleaning composition. Thus, the most preferred size of sheets for use in the present invention range from about 4" X 14", particularly from about 5" X 12" to about 9" X 10". In conjunction therewith, the preferred sheets have surface areas ranging from about 12 inches squared to about 224 inches squared, and most preferably from about 48 inches squared to about 120 inches squared.

The dry-cleaning composition of the present invention is released from the sheet, sponge, dauber, stick, cube, granules, etc. upon

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physical contact with the fabric articles, e.g., as when the fabric articles and the sheet, sponge, dauber, stick, cube, granules, etc. are tumbled together in the bag, preferably under heated
5 conditions.

For instance, in one embodiment of the invention, one or more fabric articles and a suitably sized, impregnated, flexible sheet are placed into the bag, the bag is closed, and then
10 the bag is subjected to an amount of agitation and/or heat effective to release the anhydrous dry-cleaning composition from the flexible sheet upon contacting the fabric articles. The sheet "tumbles" among the fabric articles, thus
15 dispersing the composition evenly onto them. Thus contacted, the fabric articles are cleaned, freshened or otherwise treated by the composition.

In a preferred aspect of the invention, the closed bag, containing the flexible sheet and the fabric article(s), can be placed in a rotary
20 hot air clothes dryer to provide the effective amount of heat and/or agitation, or tumbling, usually at a temperature of about 40°-95° C., preferably at about 50°-90° C, for preselected
25 periods of time. For example, about 15-45 minutes of tumbling are sufficient to release the dry-cleaning composition from the sheet interior surface of the bag at these temperatures and to clean or freshen the fabric articles.

In an alternative embodiment of the present method, the dry-cleaning composition may further be applied directly to the soiled fabric to be cleaned, e.g., by spraying, rolling on wet or sprinkling via dry powder, the dry-cleaning
30 composition onto the fabric, the fabric subsequently placed into the bag, the bag sealed and rotated in a hot air clothes dryer.
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Where the bag has an interior surface containing the dry-cleaning composition releasably absorbed thereinto, the spotted and/or stained sections of the fabric may be manually rubbed on the inside of the impregnated bag to pre-treat the soiled areas with the dry-cleaning compositions in order to loosen the soil. In such an embodiment of the invention, the dry cleaning composition cleans the soil from the fabric while excess moisture and the removed soil are absorbed by the interior absorptive surface of the bag.

F. Bag

In order to effectively contain the liquid or vaporous dry-cleaning compositions within the confines of the sealed bag, the bag must be fabricated of an essentially gas impermeable material and comprise an opening which can be reversibly closed. The bags of the present invention may be formed from any flexible material which exhibits sufficient thermal stability for use in the rotary hot air dryer discussed above. In addition, it is important that the containment bag will not substantially be damaged upon exposure to conditions including a temperature effective to cause release of the dry-cleaning composition from the substrate, fabric, etc.

Preferably, the bag will be formed from non-porous plastic film, non-woven fabric, and the like. For example, the outermost layer of the bag can be formed from polyethylene, polypropylene, polyamide, nylon, or a multiple or layered complex comprising such materials. In a preferred embodiment, the bag of the present invention is formed by the co-extrusion of materials with the desired properties.

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Preferably the bags suitable for use in the present invention will have dimensions ranging from about 18" x 23" up to about 36" x 40". The most preferred size of bag for use in the present invention range is from about 20" x 28" to about 26" x 30". These dimensions preferably result in the bag having a surface area in the range of about 1120.in², and most preferably from about 1120 in² to about 1560 in².

For the embodiments of the invention wherein the bag has an interior surface, and at least a portion of the interior surface has an effective amount of a dry-cleaning composition releasably absorbed thereinto, the bag may be formed as above, except that it should have interior layer capable of absorbing releasably therein a sufficient amount of the gelled or liquid dry-cleaning composition to effectively clean fabrics without significant leaking or bleeding of the composition into the interior of the bag upon storage. In order to effectively contain the vaporous dry-cleaning compositions within the interior space of the sealed bag, the bag must, of course, have an essentially gas impermeable material as its outermost layer and comprise an opening which can be reversibly closed. For example, the outermost layer of the bag can be formed from polyethylene, polypropylene, polyamide, nylon or a multiple or layered complex comprising such materials. Preferably, the innermost plastic layer will be a reticulated plastic film formed in situ, a solid granular or porous absorbent solid filled plastic film or a combination of both foamed and solids loaded plastic. Examples of such materials include, but are not limited to, polyethylene, diatomaceous earth filled polyethylene.

polypropylene, and other solid absorbents dispersed in film.

In this embodiment, the bag may be formed in two steps. The thermally stable outer layer of the bag is pre-formed and a non-woven fabric subsequently attached to the inside surface of the bag in a second step.

Non-woven cloth materials useful in the present invention to form the absorbent interior surface of the bag are generally adhesively or thermally bonded fibrous products having a web or corded fiber structure, or those which comprise fibrous mats in which the fibers are distributed haphazardly or in a random array. The fibers can be natural, such as wool, silk, jute, hemp, cotton, linen, sisal, or ramie; or synthetic such as rayon, cellulose ester, polyvinyl derivatives, polyolefins, polyamides or polyesters. Generally, any diameter or denier of fiber is useful in the present invention. The non-woven cloth materials employed herein are not prone to tear or separate when used, for example, in an automatic dryer, due to the haphazard or random array of fibers in the non-woven material which impart excellent strength in all directions. Some examples of preferred non-woven cloth material useful as substrates in the present invention include 100% rayon sheets, available as described above.

The interior surface of the bag that retains the cleaning composition may be rendered suitably absorptive by a number of means. For example, the bag may have one or more multiple layers of plastic film, the innermost film being absorptive, i.e., a reticulated plastic foam, a solid granular or porous absorbent solid filled plastic film or a combination of both foamed and solids loaded plastic. Such bags may be formed by

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co-extruding one or more multiple layers of plastic layers simultaneously during the blowing of the bag. In another embodiment of the invention, a single-use dry cleaning bag is provided in which the interior surface of the bag may be pre-impregnated with the dry cleaning composition. For example, in this embodiment of the invention, the interior absorptive surface may be a non-woven fabric attached to the inside surface of the bag after formation of the bag itself, as a second step. The dry-cleaning composition may be applied to the interior absorptive surface of the bag wall, i.e., by spraying, after the manufacture of the bag. Once the dry cleaning composition has been applied, the soiled fabric can be introduced into the bag, the bag fastened and tumbled in a clothes dryer.

After use, the bag may be discarded, or if desired, it may be constructed of a suitable material to allow repeated usage in a plurality of cleaning cycles.

Examples

The following examples further illustrate the present invention and preferred embodiments thereof. It is to be understood, however, that these examples are for illustrative purposes only and are not intended to limit the scope of the specification or claims thereof in any way.

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Example I: Anhydrous Dry-Cleaning Composition

	Ingredients	wt. %
	Tripropylene glycol methyl ether	
5	(Arcosolv TPM)	71.38
	Dipropylene glycol n-butyl ether	
	(Arcosolv DPNB)	22.78
	Polysulfonic acid (HSP-1180)	2.27
	Water	3.03
10	Surfactant (Tergitol 15-S-3)	<u>0.54</u>
		100.00

In a suitable vessel, the tripropylene glycol methyl ether was charged. To this solvent, the water was added and mixed. Then the polysulfonic acid was added. The system was mixed at room temperature until the polysulfonic acid dissolved into the formulation. (Optionally, to accelerate the dissolution of the polysulfonic acid, the formulation can be warmed to 35°C with continued agitation.) Dissolution was completed in several hours.

The surfactant was added with agitation. Finally, the dipropylene glycol n-butyl ether was added slowly. The resultant mixture was a clean sparkling solution having a viscosity similar to a medium molecular weight polymer solution. Optionally, the pH of the final formula can be adjusted as desired with dilute solution of sodium or potassium hydroxide.

When tested on 100% acetate fabric, this composition cleaned and freshened the fabric while leaving virtually no visible ring or white solid residue.

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Example II: Anhydrous Dry-Cleaning Composition

Ingredients	wt. %
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	Tripropylene glycol methyl ether	
	(Arcosolv TPM)	83.73
	(2-(2-ethoxy)ethoxy)ethanol	
	(Carbitol)	9.77
5	Polysulfonic acid (HSP-1180)	5.00
	Surfactant (Igepal CO-660)	0.70
	Fragrance	0.50
	Surfactant (Tergitol 15-S-3)	<u>0.30</u>
		100.00

10 In a suitable vessel, the tripropylene glycol methyl ether was charged. To this solvent, the polysulfonic acid was added. The system was mixed at room temperature until the polysulfonic acid dissolved into the formulation. (Optionally, 15 to accelerate the dissolution of the polysulfonic acid, the formulation can be warmed to 35°C with continued agitation.) Dissolution was completed in several hours.

20 The surfactants were added with agitation. The (2-(2-ethoxy)ethoxy)ethanol was added slowly, then the fragrance. Optionally, the pH of the final formula can be adjusted as desired with dilute solution of sodium or potassium hydroxide.

25 When tested on 100% acetate fabric, this composition cleaned and freshened the fabric while leaving virtually no visible ring or white solid residue.

30 Example III: Application of the Dry-Cleaning Composition

35 The mixture of Examples I or II can be coated warm or cool onto a substrate by means of a Meyer rod, a floating knife or doctor blade. Alternatively, the substrate can be dipped into the liquid mixture or the mixture can be sprayed or sponged onto the substrate and then allowed to

thicken. The mixture remains moist on the substrate. For example, the substrate can be placed on a level surface, such as on a glass plate. The dry-cleaning reaction mixture is poured across the top of the substrate and a metal rod is drawn down the surface of the substrate, which will drive the mixture through a porous substrate. Therefore, the substrate is both impregnated with and overcoated with the dry-cleaning composition.

The finished substrates (e.g., flexible sheets, sponges, cubes, sticks, granules, daubers, etc.) on which the dry-cleaning composition is applied are preferably packaged in moisture impermeable packaging, e.g., in foil, a foil-plastic film or a foil-treated paper composite envelope.

Example III: Application of the Dry-Cleaning Composition

The dry-cleaning composition of Example I or II can be applied onto the inner absorptive surface of the bag, as by spraying, sponging or other known methods of application and then allowed to absorb into the surface.

For the embodiments of the invention wherein the bag has an interior surface, and at least a portion of the interior surface has an effective amount of a dry-cleaning composition releasably absorbed thereinto, the dry-cleaning composition may be impregnated into the inner surface of the bag during manufacturing. This embodiment of the invention provides a single use dry cleaning bag. If impregnated, the impregnation step would be achieved, for example, by spraying the dry-cleaning composition onto the absorptive inner surface of the bag during the

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'cool-down' step of manufacturing, i.e., that step when air is pumped into the bag to cool it after extrusion. The dry-cleaning composition may further be applied directly to the soiled fabric to be cleaned, i.e., by spraying, sponging or dipping, prior to introducing the fabric into the bag.

Following a cooling period, the finished dry-cleaning bags are preferably packaged in moisture impermeable packaging, e.g., in foil, a foil-plastic film or a foil-treated paper composite envelope.

The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A dry-cleaning system adapted for dry-cleaning or fabric-freshening a fabric article, comprising an effective amount of a dry-cleaning composition consisting essentially of
at least 1 water-miscible or partially water-miscible organic solvent;
polysulfonic acid; and
an effective amount of water to disperse the polysulfonic acid, where the amount of water does not exceed about 10 weight percent of the total dry-cleaning composition.
2. The dry-cleaning system of claim 1, wherein the organic solvent is selected from the group consisting of glycol ethers, liquid polyethylene glycols, C*2-C*4 polyols, and mixtures thereof.
3. The dry-cleaning system of claim 1, wherein the at least 1 organic solvent is selected from the group consisting of dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, tripropylene glycol methyl ether, 3-methoxy-3-methyl-1-butanol and γ -butyrolactone.
4. The dry-cleaning system of claim 1, wherein the dry-cleaning composition contains between about 85 and about 98.5 weight percent of the at least 1 organic solvent.
5. The dry-cleaning system of claim 1, wherein the dry-cleaning composition contains between about .5 and about 5 weight percent polysulfonic acid.

6. The dry-cleaning system of claim 1, wherein the dry-cleaning composition contains between about 1 and about 6 weight percent water.

7. The dry-cleaning system of claim 1, wherein the fabric article contains acetate, rayon, silk, or blends thereof.

8. The dry-cleaning system of claim 1, wherein the dry-cleaning composition further includes surfactants.

9. The dry-cleaning system of claim 8, wherein the surfactants are present in the dry-cleaning composition in an amount between about .01 and about 10 weight percent.

10. The dry-cleaning system of claim 1, wherein the dry-cleaning composition further includes gelling agents or viscosity modifiers.

11. The dry-cleaning system of claim 1, wherein the dry-cleaning composition further includes an agent selected from the group consisting of fabric-softening agents, anti-creasing agents, anti-soil agents, bacteriostatic agents, brightening agents, bodying agents, dyes, fiber emollients, finishing agents, fragrances, germicides, lubricants, mildew-proofing agents, moth-proofing agents, shrinkage controllers, sizing agents, and mixtures thereof.

12. The dry-cleaning system of claim 1, wherein the dry-cleaning composition further includes a compound having a vapor tension of less than or equal to 4 Pa at 25°C, which is selected from the group consisting of C₁₀-C₁₂ aliphatic

alcohols, C₁₀-C₁₃ aldehydes, C₁₃-C₁₈ aliphatic ketones, aromatic ketones having a musk odor and up to 18 carbon atoms, C₈-C₁₅ aliphatic esters, methyl anthranilate, methyl N-methylantranilate, p-cresyl phenylacetate, amyl salicylate, coumarin, dihydrocoumarin, gammadecalactone, dodecalactone, undecalactone, eugenol, isoeugenol, diphenyl oxide, the methyl and ethyl ethers of naphthol, galaxolide, indole and its reaction products with hydroxycitronella, tridecene-2-nitrile, and 2-(2'-methyl-pent-2'-enyl)-5-methyl pyridine.

13. The dry-cleaning system of claim 12, wherein the amount of the compound present in the dry-cleaning composition is between about .2 to about 5 weight percent.

14. The dry-cleaning system of claim 1, wherein the dry-cleaning composition consists essentially of about 95% of the at least 1 non-polar organic solvent, about 2.5% of polysulfonic acid, and about 2.5% water.

15. The dry-cleaning system of claim 1, wherein the dry-cleaning composition is present on a substrate.

16. The dry-cleaning system of claim 15, wherein the substrate is selected from the group consisting of a sheet, a sponge, a dauber, a stick, granules or a cube.

17. The dry-cleaning system of claim 1, wherein the dry-cleaning composition is present in a spray or roll on solution.

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18. The dry-cleaning system of claim 16, wherein the substrate is a sheet.

19. The dry-cleaning system of claim 1 which further includes a bag including an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner.

20. The dry-cleaning system of claim 19, wherein the bag has an interior surface, and at least a portion of the interior surface has an effective amount of the dry-cleaning composition releasably absorbed therein, wherein the bag is formed of a flexible non-porous material which is not substantially damaged upon exposure to agitation and to a temperature effective to cause the release of the dry-cleaning composition from the interior surface.

21. A process for cleaning or freshening a soiled fabric article with a dry-cleaning composition, the process comprising:

(a) placing into a bag the soiled fabric article and an effective amount of the dry-cleaning composition of claim 1,

wherein the bag includes an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner;

(b) closing the fastening system to form the bag into an effective closed system comprising the soiled fabric article and the dry-cleaning composition;

(c) tumbling the closed system in a rotary clothes dryer at an elevated temperature, so that the dry-cleaning composition contacts the

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soiled fabric article so as to effectively disperse the soil; and

(d) opening the fastening system and removing the cleaned or freshened fabric article from the bag.

22. The process of claim 21, wherein the dry-cleaning composition is present on a substrate.

23. The process of claim 22, wherein the substrate is selected from the group consisting of a sheet, a sponge, a dauber, a stick, granules and a cube.

24. The process of claim 23, wherein the substrate is a sheet.

25. The process of claim 21, wherein the organic solvent is selected from the group consisting of glycol ethers, liquid polyethylene glycols, C*2-C*4 polyols, and mixtures thereof.

26. The process of claim 21, wherein the at least 1 organic solvent is selected from the group consisting of dipropylene glycol n-propyl ether, dipropylene glycol n-butyl ether, tripropylene glycol methyl ether, 3-methoxy-3-methyl-1-butanol and γ butyrolactone.

27. The process of claim 21, wherein the dry-cleaning composition contains between about 85 and about 98.5 weight percent of the at least 1 organic solvent.

28. The process of claim 21, wherein the dry-cleaning composition contains between

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about .5 and about 5 weight percent polysulfonic acid.

29. The process of claim 21, wherein the dry-cleaning composition contains between about 1 and about 6 weight percent water.

30. The process of claim 21, wherein the fabric article contains acetate, rayon, silk, or blends thereof.

31. The process of claim 21, wherein the dry-cleaning composition further includes surfactants.

32. The process of claim 31, wherein the surfactants are present in the dry-cleaning composition in an amount between about .01 and about 10 weight percent.

33. The process of claim 21, wherein the dry-cleaning composition further includes gelling agents or viscosity modifiers.

34. The process of claim 21, wherein the dry-cleaning composition further includes an agent selected from the group consisting of fabric-softening agents, anti-creasing agents, anti-soil agents, bacteriostatic agents, brightening agents, bodying agents, dyes, fiber emollients, finishing agents, fragrances, germicides, lubricants, mildew-proofing agents, moth-proofing agents, shrinkage controllers, sizing agents, and mixtures thereof.

35. The process of claim 21, wherein the dry-cleaning composition further includes a

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compound having a vapor tension of less than or equal to 4 Pa at 25°C, which is selected from the group consisting of C₁₀-C₁₂ aliphatic alcohols, C₁₀-C₁₃ aldehydes, C₁₃-C₁₈ aliphatic ketones, aromatic ketones having a musk odor and up to 18 carbon atoms, C₈-C₁₅ aliphatic esters, methyl anthranilate, methyl N-methylanthranilate, p-cresyl phenylacetate, amyl salicylate, coumarin, dihydrocoumarin, gammadecalactone, dodecalactone, undecalactone, eugenol, isoeugenol, diphenyl oxide, the methyl and ethyl ethers of naphthol, galaxolide, indole and its reaction products with hydroxycitronella, tridecene-2-nitrile, and 2-(2'-methyl-pent-2'-enyl)-5-methyl pyridine.

36. The process of claim 21, wherein the dry-cleaning composition consists essentially of about 95% of the at least 1 organic solvent, about 2.5% of polysulfonic acid, and about 2.5% water.

37. The process of claim 35, wherein the amount of the compound present in the dry-cleaning composition is between about .2% to about 5%.

38. The process of claim 21, wherein the dry-cleaning composition is present in a spray or roll on solution.

39. The process of claim 21, wherein the bag has an interior surface, and at least a portion of the interior surface has an effective amount of the dry-cleaning composition releasably absorbed thereinto, wherein the bag is formed of a flexible non-porous material which is not substantially damaged upon exposure to agitation

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and to a temperature effective to cause the release of the dry-cleaning composition from the interior surface.

40. A method for removing a stain from a soiled fabric article, the method comprising the steps of:

(a) placing into a bag the soiled fabric article and an effective amount of the dry-cleaning composition of claim 1,

wherein the bag includes an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner;

(b) closing the fastening system to form the bag into an effective closed system comprising the soiled fabric article and the dry-cleaning composition;

(c) tumbling the closed system in a rotary clothes dryer at an elevated temperature, so that the dry-cleaning composition contacts the soiled fabric article so as to effectively disperse the stain; and

(d) opening the fastening system and removing the cleaned fabric article from the bag.

41. The method of claim 40 wherein, prior to step (a), an amount of the dry-cleaning composition is applied to the soiled fabric article to loosen the stain.

42. The method of claim 41, wherein the amount of dry-cleaning composition prior to step (a) is applied by rubbing or dabbing the soiled fabric article with the dry-cleaning composition so as to loosen and remove stain from the soiled fabric article.

43. The method of claim 41, wherein the amount of dry-cleaning composition prior to step (a) is applied either by spraying, rolling on or dipping the soiled fabric article with the dry cleaning composition.

44. A kit for dry-cleaning or fabric-freshening a fabric article, comprising

(i) an effective amount of the dry-cleaning composition of claim 1,

and

(ii) a bag including an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner.

45. A dry-cleaning system adapted for dry-cleaning or fabric-freshening a fabric article, comprising an effective amount of a dry-cleaning composition consisting essentially of polysulfonic acid; and

at least 1 organic solvent, which is capable of dispersing the polysulfonic acid in the absence of a sufficient amount of water,

wherein the dry-cleaning composition does not contain more than about 1 weight percent water.

46. The dry-cleaning system of claim 45, wherein the at least 1 organic solvent is selected from the group consisting of tripropylene glycol methyl ether and (2-(2-ethoxy)ethoxy)ethanol.

47. The dry-cleaning system of claim 45, wherein the dry-cleaning composition contains

between about 90 and about 99.9 weight percent of the at least 1 organic solvent.

48. The dry-cleaning system of claim 45, wherein the dry-cleaning composition contains between about 0.1 and about 10 weight percent of polysulfonic acid.

49. The dry-cleaning system of claim 45, wherein the fabric article contains acetate, rayon, silk, or blends thereof.

50. The dry-cleaning system of claim 45, wherein the dry-cleaning composition further contains surfactants.

51. The dry-cleaning system of claim 45, wherein the dry-cleaning composition further includes gelling agents or viscosity modifiers.

52. The dry-cleaning system of claim 45, wherein the dry-cleaning composition further includes an agent selected from the group consisting of fabric-softening agents, anti-creasing agents, anti-soil agents, bacteriostatic agents, brightening agents, bodying agents, dyes, fiber emollients, finishing agents, fragrances, germicides, lubricants, mildew-proofing agents, moth-proofing agents, shrinkage controllers, sizing agents, and mixtures thereof.

53. The dry-cleaning system of claim 45, wherein the dry-cleaning composition further includes a compound having a vapor tension of less than or equal to 4 Pa at 25°C, which is selected from the group consisting of C₁₀-C₁₂ aliphatic alcohols, C₁₀-C₁₃ aldehydes, C₁₃-C₁₈ aliphatic

ketones, aromatic ketones having a musk odor and up to 18 carbon atoms, C₈-C₁₅ aliphatic esters, methyl anthranilate, methyl N-methylantranilate, p-cresyl phenylacetate, amyl salicylate, coumarin, dihydrocoumarin, gammadecalactone, dodecalactone, undecalactone, eugenol, isoeugenol, diphenyl oxide, the methyl and ethyl ethers of naphthol, galaxolide, indole and its reaction products with hydroxycitronella, tridecene-2-nitrile, and 2-(2'-methyl-pent-2'-enyl)-5-methyl pyridine.

54. The dry-cleaning system of claim 45, wherein the dry-cleaning composition consists essentially of about 95% of the at least 1 organic solvent, and about 5% of the polysulfonic acid.

55. The dry-cleaning system of claim 53, wherein the dry-cleaning composition contains between about .2 and about 5 weight percent of the compound.

56. The dry-cleaning system of claim 45, wherein the dry-cleaning composition is present on a substrate.

57. The dry-cleaning system of claim 56, wherein the substrate is selected from the group consisting of a sheet, a sponge, a dauber, a stick, granules or a cube.

58. The dry-cleaning system of claim 45, wherein the dry-cleaning composition is present in a spray or roll on solution.

59. The dry-cleaning system of claim 57, wherein the substrate is a sheet.

60. The dry-cleaning system of claim 45 which further includes a bag including an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner.

61. The dry-cleaning system of claim 60, wherein the bag has an interior surface, and at least a portion of the interior surface has an effective amount of the dry-cleaning composition releasably absorbed therein, wherein the bag is formed of a flexible non-porous material which is not substantially damaged upon exposure to agitation and to a temperature effective to cause the release of the dry-cleaning composition from the interior surface.

62. A process for cleaning or freshening a soiled fabric article with a dry-cleaning composition, the process comprising:

(a) placing into a bag the soiled fabric article and an effective amount of the dry-cleaning composition of claim 45,

wherein the bag includes an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner;

(b) closing the fastening system to form the bag into an effective closed system comprising the soiled fabric article and the dry-cleaning composition;

(c) tumbling the closed system in a rotary clothes dryer at an elevated temperature, so that the dry-cleaning composition contacts the soiled fabric article so as to effectively disperse the soil; and

(d) opening the fastening system and removing the cleaned or freshened fabric article from the bag.

63. The process of claim 62, wherein the dry-cleaning composition is present on a substrate.

64. The process of claim 63, wherein the substrate is selected from the group consisting of a sheet, a sponge, a dauber, a stick, granules and a cube.

65. The process of claim 64, wherein the substrate is a sheet.

66. The process of claim 62, wherein the at least 1 organic solvent is selected from the group consisting of tripropylene glycol methyl ether and (2-(2-ethoxy)ethoxy)ethanol.

67. The process of claim 62, wherein the dry-cleaning composition contains between about 90 and about 99.9 weight percent of the at least 1 organic solvent.

68. The process of claim 62, wherein the dry-cleaning composition contains between about 0.1 and about 10 weight percent of the polysulfonic acid.

69. The process of claim 62, wherein the dry-cleaning composition consists essentially of about 95 weight percent organic solvent and about 5 weight percent polysulfonic acid.

70. The process of claim 62, wherein the dry-cleaning composition further includes gelling agents or viscosity modifiers.

71. The process of claim 62, wherein the dry-cleaning composition further includes an agent selected from the group consisting of fabric-softening agents, anti-creasing agents, anti-soil agents, bacteriostatic agents, brightening agents, bodying agents, dyes, fiber emollients, finishing agents, fragrances, germicides, lubricants, mildew-proofing agents, moth-proofing agents, shrinkage controllers, sizing agents, and mixtures thereof.

72. The process of claim 62, wherein the dry-cleaning composition further includes a compound having a vapor tension of less than or equal to 4 Pa at 25°C, which is selected from the group consisting of C₁₀-C₁₂ aliphatic alcohols, C₁₀-C₁₃ aldehydes, C₁₃-C₁₈ aliphatic ketones, aromatic ketones having a musk odor and up to 18 carbon atoms, C₈-C₁₅ aliphatic esters, methyl anthranilate, methyl N-methylantranilate, p-cresyl phenylacetate, amyl salicylate, coumarin, dihydrocoumarin, gammadecalactone, dodecalactone, undecalactone, eugenol, isoeugenol, diphenyl oxide, the methyl and ethyl ethers of naphthol, galaxolide, indole and its reaction products with hydroxycitronella, tridecene-2-nitrile, and 2-(2'-methyl-pent-2'-enyl)-5-methyl pyridine.

73. The process of claim 72, wherein the dry-cleaning composition contains about .2% to about 5% of the compound.

74. The process of claim 62, wherein the dry-cleaning composition is present in a spray or roll on solution.

75. The process of claim 62, wherein the bag has an interior surface, and at least a portion of the interior surface has an effective amount of the dry-cleaning composition releasably absorbed thereinto, wherein the bag is formed of a flexible non-porous material which is not substantially damaged upon exposure to agitation and to a temperature effective to cause the release of the dry-cleaning composition from the interior surface.

76. A method for removing a stain from a soiled fabric article, the method comprising the steps of:

(a) placing into a bag the soiled fabric article and an effective amount of the dry-cleaning composition of claim 45,

wherein the bag includes an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner;

(b) closing the fastening system to form the bag into an effective closed system comprising the soiled fabric article and the dry-cleaning composition;

(c) tumbling the closed system in a rotary clothes dryer at an elevated temperature, so that the dry-cleaning composition contacts the soiled fabric article so as to effectively disperse the stain; and

(d) opening the fastening system and removing the cleaned fabric article from the bag.

77. The method of claim 76 wherein, prior to step (a), an amount of the dry-cleaning composition is applied to the soiled fabric article to loosen the stain.

78. The method of claim 77, wherein the amount of dry-cleaning composition prior to step (a) is applied by rubbing or dabbing the soiled fabric article with the dry-cleaning composition so as to loosen and remove stain from the soiled fabric article.

79. The method of claim 77, wherein the amount of dry-cleaning composition prior to step (a) is applied either by spraying, rolling on or dipping the soiled fabric article with the dry cleaning composition.

80. The dry-cleaning system of claim 62, wherein the fabric article contains acetate, rayon, silk, or blends thereof.

81. A kit for dry-cleaning or fabric-freshening a fabric article, comprising

(i) an effective amount of the dry-cleaning composition of claim 45,

and

(ii) a bag including an opening comprising a fastening system so that the bag can enclose the soiled fabric article in an effective vapor impermeable manner.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/20619

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D06L1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 238 587 A (SMITH JAMES A ET AL) 24 August 1993 cited in the application see the whole document ---	1-4, 6-27, 29-47, 49-67, 69-81
A	US 4 336 024 A (ROSSARD JEAN-CLAUDE ET AL) 22 June 1982 cited in the application see the whole document ---	1-4, 6-27, 29-47, 49-67, 69-81
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Saunders, T

INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 96 30582 A (PROCTER & GAMBLE) 3 October 1996</p> <p>see examples</p>	<p>1, 15-25, 27, 29-32, 34, 36, 39-44, 56-67, 69, 71, 74-81</p>
A	<p>GB 2 302 553 A (RECKITT & COLMAN INC) 22 January 1997</p> <p>see page 16, line 13 - line 17 see page 17, line 12 - line 15; claims 1-11</p>	<p>1, 15, 16, 19, 21-23, 25, 30-34, 40, 44, 56, 57, 60, 62-64, 70, 71, 76, 80, 81</p>
A	<p>EP 0 479 146 A (MIHAMA CORP) 8 April 1992</p> <p>see claims 1-4</p>	<p>1, 2, 4, 6, 7, 45, 47, 49</p>
A	<p>WO 94 18300 A (ROGERS NEIL ; WITHERS PAUL) 18 August 1994</p> <p>see abstract; example 1</p>	<p>1, 5, 14, 36, 45, 48, 54</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/20619

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5238587 A	24-08-1993	CA 2135746 A EP 0640156 A JP 7509629 T WO 9323603 A	25-11-1993 01-03-1995 26-10-1995 25-11-1993
US 4336024 A	22-06-1982	AT 7054 T EP 0036833 A PT 72541 B	15-04-1984 30-09-1981 10-02-1982
WO 9630582 A	03-10-1996	US 5547476 A CA 2216753 A EP 0817879 A	20-08-1996 03-10-1996 14-01-1996
GB 2302553 A	22-01-1997	AU 6284296 A AU 6284396 A AU 6387496 A CA 2224692 A CA 2224693 A CA 2224794 A EP 0843603 A EP 0842318 A EP 0833976 A GB 2302878 A GB 2302879 A WO 9700993 A WO 9700738 A WO 9700990 A AU 6335696 A GB 2310796 A WO 9733029 A	22-01-1997 22-01-1997 22-01-1997 09-01-1997 09-01-1997 09-01-1997 27-05-1998 20-05-1998 08-04-1998 05-02-1997 05-02-1997 09-01-1997 09-01-1997 09-01-1997 22-09-1997 10-09-1997 12-09-1997
EP 0479146 A	08-04-1992	JP 4142398 A DE 69123683 D DE 69123683 T ES 2097173 T US 5634947 A	15-05-1992 30-01-1997 28-05-1997 01-04-1997 03-06-1997
WO 9418300 A	18-08-1994	AU 6006994 A EP 0683812 A	29-08-1994 29-11-1995